FINAL REPORT

CONTRACT ARB-2066

SUB-MICRON PARTICULATE ANALYZER

Prepared by: Royco Instruments, Inc.
141 Jefferson Drive
Menlo Park, California 94025

Principal Investigator:
Alvin Lieberman
Director of Research

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ABSTRACT

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SUB-MICRON PARTICULATE ANALYZER

The feasibility of a continuous operation condensation nuclei counter was demonstrated. The device consisted of a system for creating a supersaturated air stream combined with a conventional ROYCO aerosol particle counter. Water and alcohol were investigated as condensing vapor sources. Temperature and vapor concentration ranges were investigated with the system, which included an expansion chamber and a diffusion chamber to achieve the required submicron particle growth. Tests were conducted using several nuclei sources.

The device was used to show the effect of residence time on gas-phase reactions that result in particle generation.

I - INTRODUCTION

This is the final report on Contract ARB-2066, Sub-Micron Particulate Analyzer for the period June 1971 to September 1972. It describes a theoretical and experimental program to determine the feasibility of a continuous condensation nuclei counter. Condensation nuclei are generally considered to be particles ranging in size from approximately 0.001μm to several microns in diameter. They are usually capable of acting as heterogeneous nuclei for vapor deposition and growth of liquid droplets.

Typically measurement of condensation nuclei is effected by subjecting a sample of air to a known supersaturation and observing the concentration of droplets which have formed and grown to visible size (a 20μm diam.) over a period of a few seconds. Supersaturation is attained either by injecting the air sample into a static diffusion chamber where known vapor gradients are established or by injecting the air into an expansion chamber where transient pressure variation causes separation by adiabatic expansion. In either case, air samples are intermittent, the sample volume is small and measurements are made over a relatively long time during a transient process. The objectives of the work described in this report were to develop feasibility of design, including establishment of optimum design parameters for an instrument that could overcome the problems mentioned above and that could be capable of quantifying particles (condensation nuclei) by number in sizes 0.01μm and larger. The hardware necessary to demonstrate the feasibility of the preliminary design was to be breadboarded. Testing to demonstrate design validity and the effect of variations in operating parameters was to be carried out. Finally, some application possibilities were to be demonstrated.

During the course of this program, a discussion of the analyzer development was prepared for presentation to the USAEC 12th Air Cleaning Conference. This paper is included as an appendix to this report.

II - SYSTEM DESIGN

A. Design Basis

In order to meet the objectives, a combination of the expansion and diffusion systems was chosen with a conventional optical single particle counter for detection after the nuclei had been activated and grown and were in a relatively stable regime. The initial activation took place during adiabatic expansion. An air sample is passed through a humidifier where the vapor content of the air is increased so that the supply for droplet growth will be adequate. The humidifier air is passed through a nozzle where adiabatic expansion cools the gas, begins the nuclei growth process and directs the sample stream into the condenser chamber. In this chamber, the droplets are grown to a stable size. The condenser chamber is cooled so as to establish a fixed temperature and vapor gradient from the sample inlet to the chamber walls. The optical particle counter is used to count the droplets after they have formed.

B. Description of Apparatus

The sub-micron particle analyzer is made of three subsystems as shown in Figure 1. The sample stream enters the humidifier first and then passes through the condenser and into the optical particle counter.

The humidifier is a Pyrex cylinder 3.3 cm in diameter and 15.0 cm long. The cylinder is mounted horizontally with a pool of liquid, either water or ethyl alcohol, filling the lower portion of the cylinder. Several tests were made with the walls of the humidifier lined with a glass wool wick; but the performance of the system was unchanged; therefore, the wick was not used in all work reported here. A Teflon encased resistance heater, used to maintain an elevated liquid temperature and vapor supply is immersed in the liquid pool. The sample stream enters the humidifier slightly above the surface of the pool and flows over the pool and exits through a vertical tube at the opposite end of the humidifier. The average sample flow rate through the system is 1.0 liters/min which gives an average residence time in the humidifier of 8 seconds.

The exit tube in the humidifier has an internal diameter of 4 mm and is 7 cm long. The end of the tube is drawn down to form an orifice 0.15 mm in diameter.

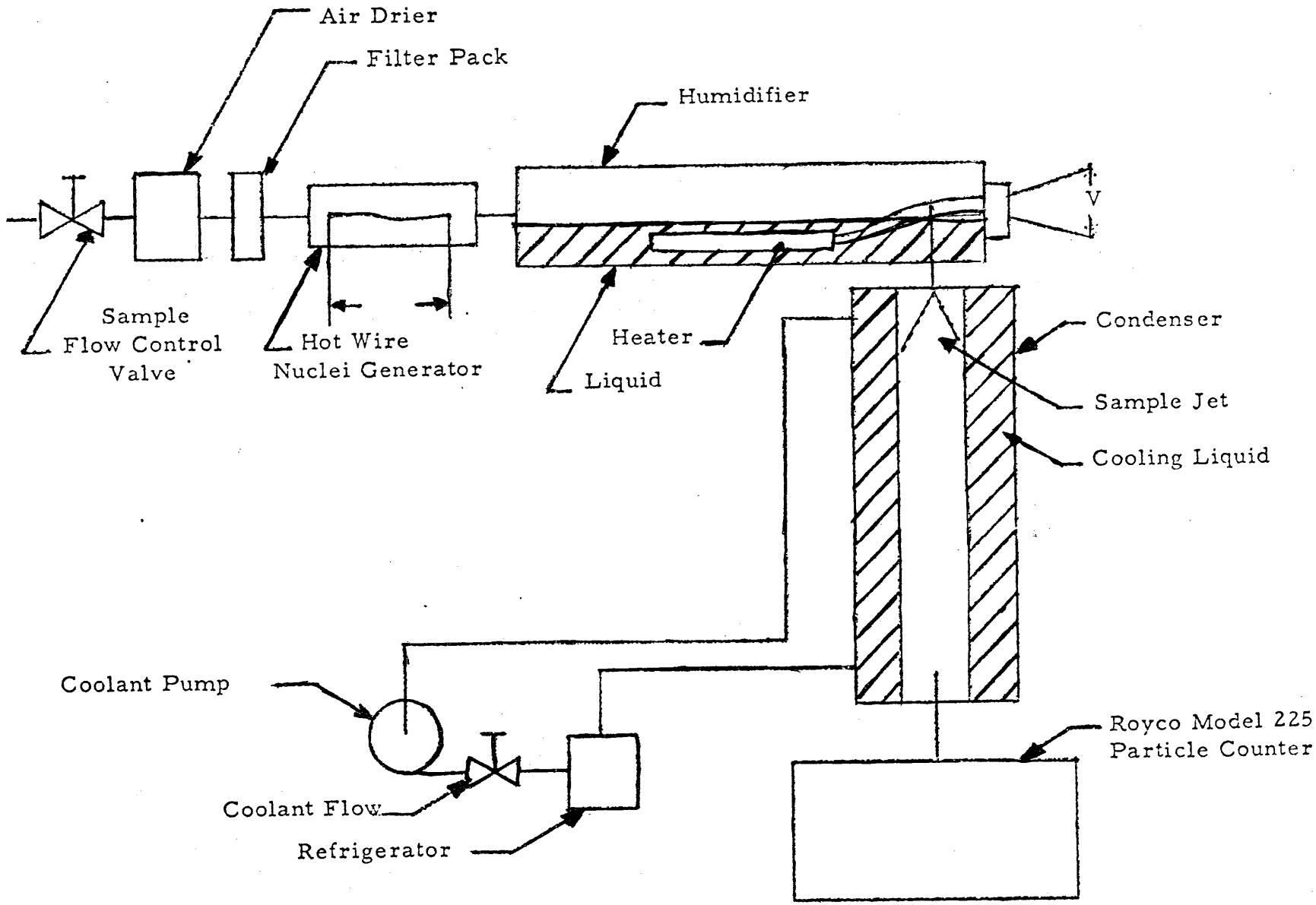

Figure 1. Condensation Nuclei Counter Schematic

B. Description of Apparatus, continued

A resistance heater is wrapped around the tube to maintain the wall temperature a few degrees higher than that of the liquid pool in the humidifier to prevent condensation on the walls of the tube. If condensation is allowed to occur, the liquid is advected into the sample stream at the orifice. The droplets thus created are counted by the optical counter thereby giving a false indication of the presence of condensation nuclei. The orifice at exit of the tube is located at the upper end of the condenser.

The condenser is a double wall Pyrex cylinder mounted vertically. The outer chamber forms an annular passage for cooling fluid, a glycol/water mixture, which is continuously circulated by an electric motor driven gear pump. The temperature of the condenser is maintained by varying the flow rate of the cooling fluid through a copper tube heat exchanger cooled by dry ice.

The sample stream enters the upper end of the condenser inner chamber as a small jet approximately .15 mm in diameter. On entering the condenser chamber the jet expands (ΔP = 1 psi) in the inner chamber which is 2.16 cm in diameter and 20 cm long. The sample stream then flows downward in laminar flow and out the lower end of the chamber. A separate flow system in the optical particle counter removes a continuous sample of 0.28 liters per minute from the chamber. The excess sample stream is allowed to exhaust to the atmosphere.

The optical particle counter, a Royco Model 225, is a forward scattered light detection device capable of detecting single particles of 0.5 micron diameter and larger. The output data from the counter is recorded graphically as total particle concentration in a given size range versus time or sample volume. The size range of condensation nuclei are much smaller than can be detected by an optical system since the individual nuclei are smaller than the wave length of light and produce negligible scattering. Therefore the purpose of the optical counter is to count the individual droplets formed around submicron particles. The apparatus described herein is a system for causing the droplets to increase in size to the place where they can be counted by a standard optical counter.

Submicron particles in the size range 0.01 to 0.1 micron change size in response to changes in humidity. At a relative humidity below 90% very little particle size change occurs except for hygroscopic nuclei which may pick up enough water vapor to double in size (Reference 1). At and above 100% relative humidity, abrupt size changes can occur due to condensation of water vapor on the surface of the particle. The degree of supersaturation required for this rapid growth is dependent on the size of the submicron particle and to a lesser extent on the chemical characteristics of the particle.

B. Description of Apparatus, continued

The change in vapor pressure as a function of the radius of a small droplet is given by the KELVIN equation.

$$\text{Ln}\,(P/Po) = \frac{2M_i \gamma}{RT \rho_l r}$$

where P = vapor pressure of droplet of radius r

Po = vapor pressure of a flat surface

M_i = molecular weight of liquid

γ = surface tension of liquid

R = gas constant

T = absolute temperature

ρ_l = liquid density

r = droplet radius

When the system is supersaturated to the extent that the pressure of the vapor surrounding the particle exceeds the vapor pressure of the droplet of radius r, additional vapor is condensed on the droplet and growth continues dependent on the time allowed and the amount of vapor available for condensation. Growth ceases when the droplet comes into equilibrium with the surrounding vapor. The degree of supersaturation is then reduced by condensation of vapor on the droplets and the temperature rise due to the latent heat of vaporization of the condensed liquid.

In the system described herein, the aerosol stream, as it passes through the humidifier, is saturated with vapor at the humidifier liquid temperature. Very little change in particle size occurs since the relative humidity remains below 100%. As the aerosol stream traverses the heated exit tube, the temperature is increased a few degrees with a corresponding small decrease in relative humidity. At the end of the tube, the aerosol stream expands through a nozzle into the condensation chamber. The expansion cause a drop in gas temperature according to the equation

$$T_2 = T_1 \left[\frac{P_2}{P_1}\right]^{\frac{k-1}{k}}$$

where 1 and 2 refer to the upstream and the downstream conditions respectively. For this system the temperature drop due to adiabatic expansion is approximately 2% which produces a small change in the degree of saturation. The walls of the condenser chamber are at a temperature which is much lower than the aerosol stream temperature. When the aerosol jet enters the condenser, it expands and flows downward toward the exit in laminar flow.

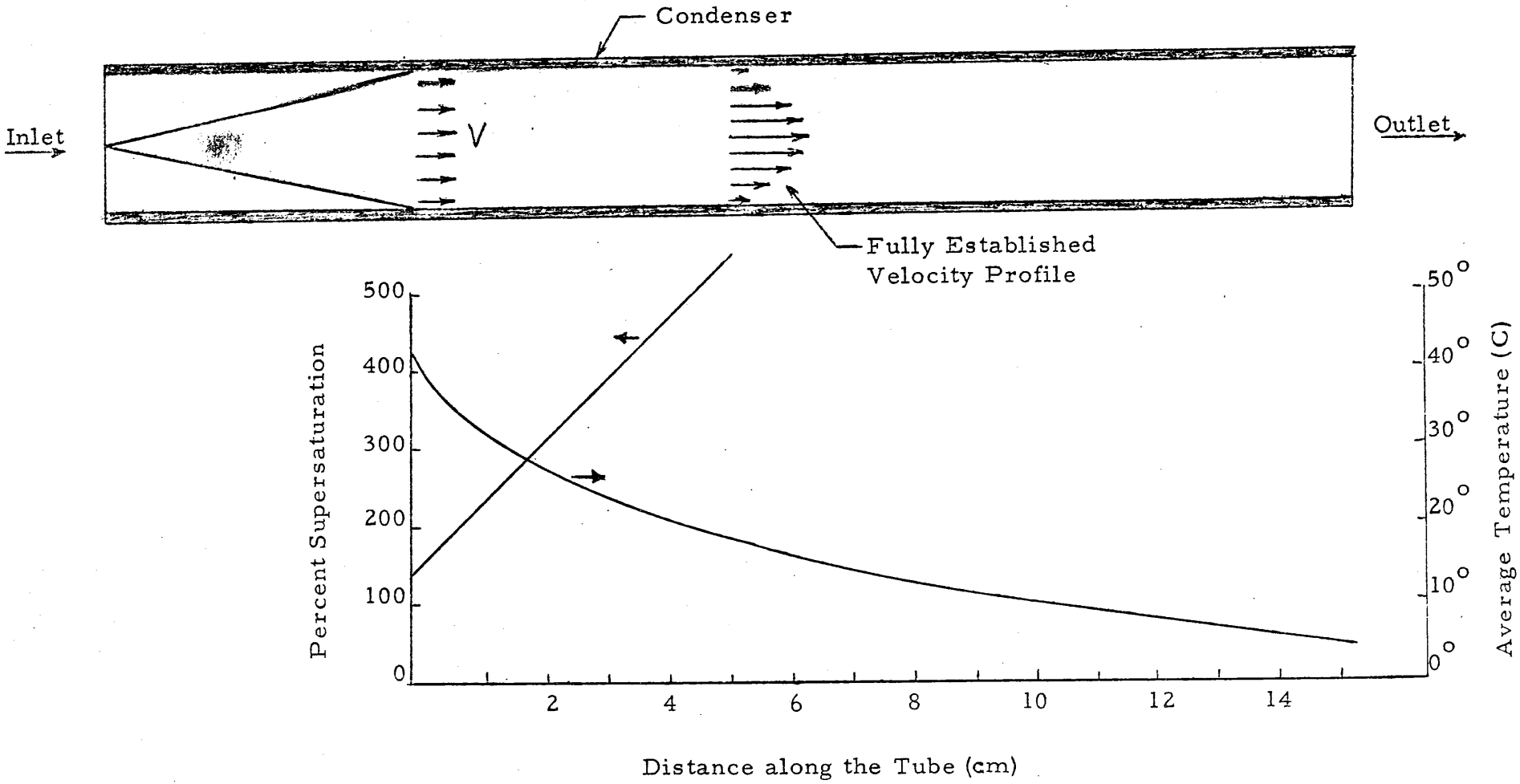

Figure 2. Flow Conditions in the Condenser

III - DATA AND DISCUSSION

A majority of the experiments were performed using an electrically heated nichrome wire as a source of submicron particles. Reference 2 states that a heated nichrome wire surrounded by clean flowing air produces high concentrations of small particles approximately 0.006 micron diameter. The aerosol used in these experiments were generated by a 0.1 mm diameter nickel-chromium (80/20) wire enclosed in a glass tube which was cooled by an external air stream.

Figure 3 shows the effect of increasing the condensable vapor in the sample stream. The aerosol generation rate was held constant by controlling the current through the nichrome wire while the vapor pressure above the liquid pool in the humidifier was varied. The vapor pressure was controlled by monitoring the temperature of the liquid. Curve A shows that as the water vapor pressure increased, the number of nuclei which were activated to form droplets also increased; i.e., smaller and smaller nuclei are activated to form droplets. However, the rate of increase of droplets falls off after a certain level of vapor pressure is reached and the curve approaches a maximum value. The maximum is created by limits on the level of supersaturation attained in the condenser rather than depletion of the nuclei available. The level of supersaturation is controlled by both the rate of heat conduction from the sample stream and the rate of diffusion of water vapor to the cold walls of the condenser.

This same experiment was repeated using ethyl alcohol as the condensable vapor instead of water. Ethyl alcohol has a diffusion coefficient which is approximately one half that of water so that less vapor is lost to the walls of the condenser as the sample stream is cooled. With the aerosol generator operating under the same conditions, higher concentrations of droplets were recorded by the optical counter. As the vapor pressure increases, curve B decreases in slope indicating again that a limit exists on the number of nuclei which can be activated. The limiting value is much higher than the corresponding value for water. It should be noted that the aerosol generator was found to fluctuate ±7% in concentration under steady operating conditions; therefore, the difference in concentration between alcohol and water is significantly greater than random variations in the aerosol generator output.

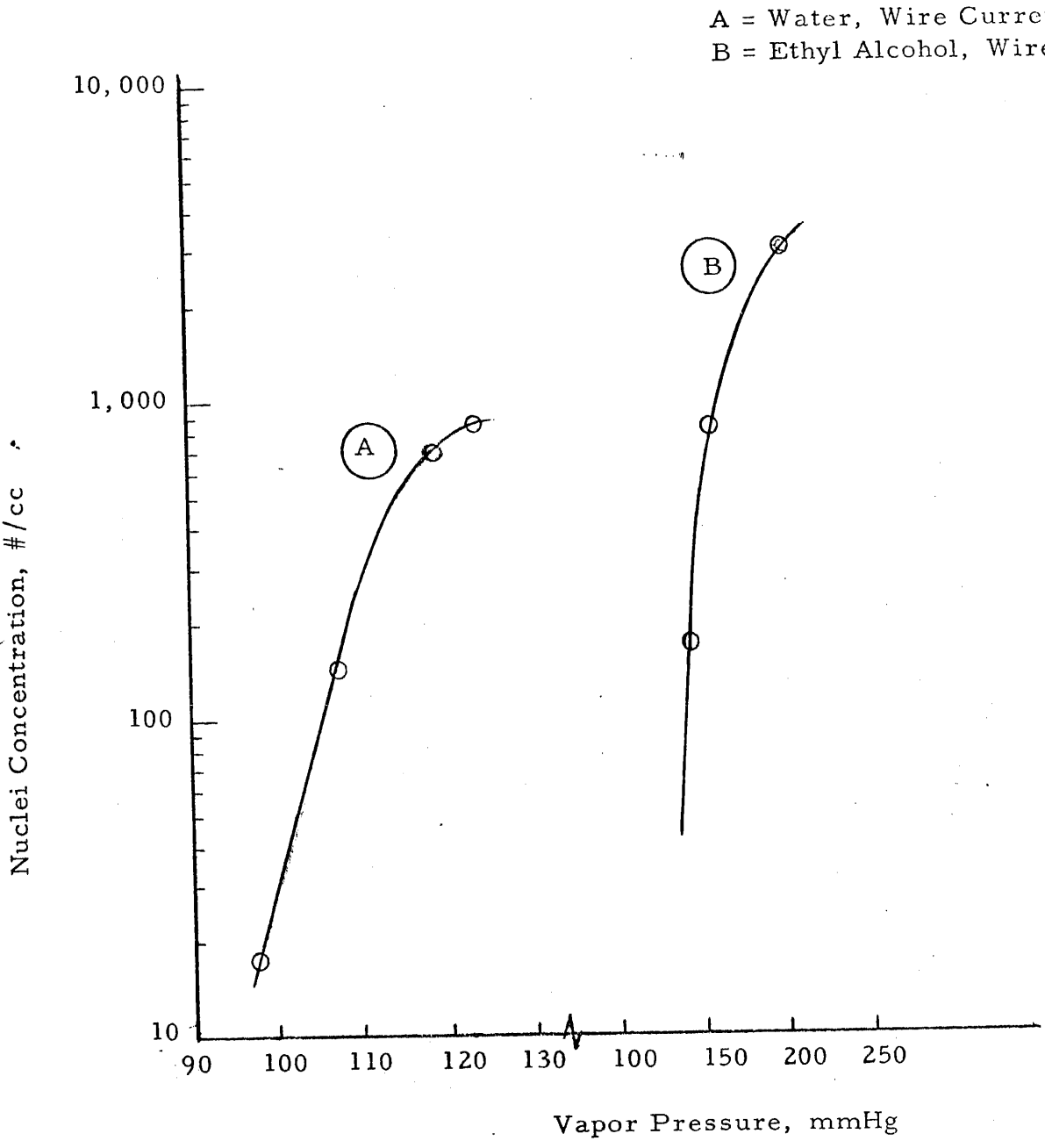

Figure 3. Nuclei Concentration as a function of Humidifier Vapor Pressure

Figure 4 shows the results of experiments where the current through the wire was varied while all the other parameters were held constant. Two different phenomena can be ascertained from these data. Curve A, for water vapor, shows that as the wire current increased, the droplet concentration increased toward a limiting value. This concentration increase is due to the generation of more large nuclei (Ref. 3) which are activated at lower levels of supersaturation. These nuclei grow to a size where they are detected by the optical counter. Three curves are shown for ethyl alcohol with different vapor pressures in the humidifier. As the vapor pressure is increased at a constant wire current (for example, 0.7 amps) the concentration of droplets increases indicating that the additional vapor in the sample stream produces a higher level of supersaturation and thus activates smaller nuclei. This is shown in Figure 3 also. For a fixed level of supersaturation, an increase in wire current results in an increase in the concentration of droplets just as with water vapor.

These results indicate that the minimum size nuclei detected by the system is regulated by the vapor content of the sample stream.

Figure 5 shows the effect of varying the sample flow rate. As the residence time decreases or the flow rate increases, the point at which the temperature profile is fully established moves further down the tube and the available time for droplet growth decreases. This causes a corresponding decrease in the number of droplets which grow to a size where they can be detected.

Table 1 shows the particle size distribution for typical droplets obtained under conditions shown below the table. These conditions are those wherein the droplets have not yet grown to an equilibrium point. Had equilibrium been attained, the activated nuclei should grow to form more or less mono-disperse droplets at sizes where, in the entering sample, there were scarcely any particles to be measured. Table 1 does, however, show an atypical particle size distribution. More larger particles are seen than would be expected in a normal aerosol.

A test was conducted to determine the response of the system to submicron particles other than the metallic particles given off by the nichrome wire. A layer of salt (NaCl) crystals was deposited on a coil of nichrome wire by allowing water to evaporate from a saturated solution. The wire coil was then placed in the aerosol generator and heated by an electric current. The results are shown in Figure 6. The concentration of droplets increased rapidly with increasing wire current. It should be noted that the temperature of the wire was much less than that required to produce metallic particles so that all the droplets were formed by submicron salt particles. Note Figure 4 which shows that essentially zero nuclei production occurred from the nichrome wire alone at wire currents under 0.7 amperes.

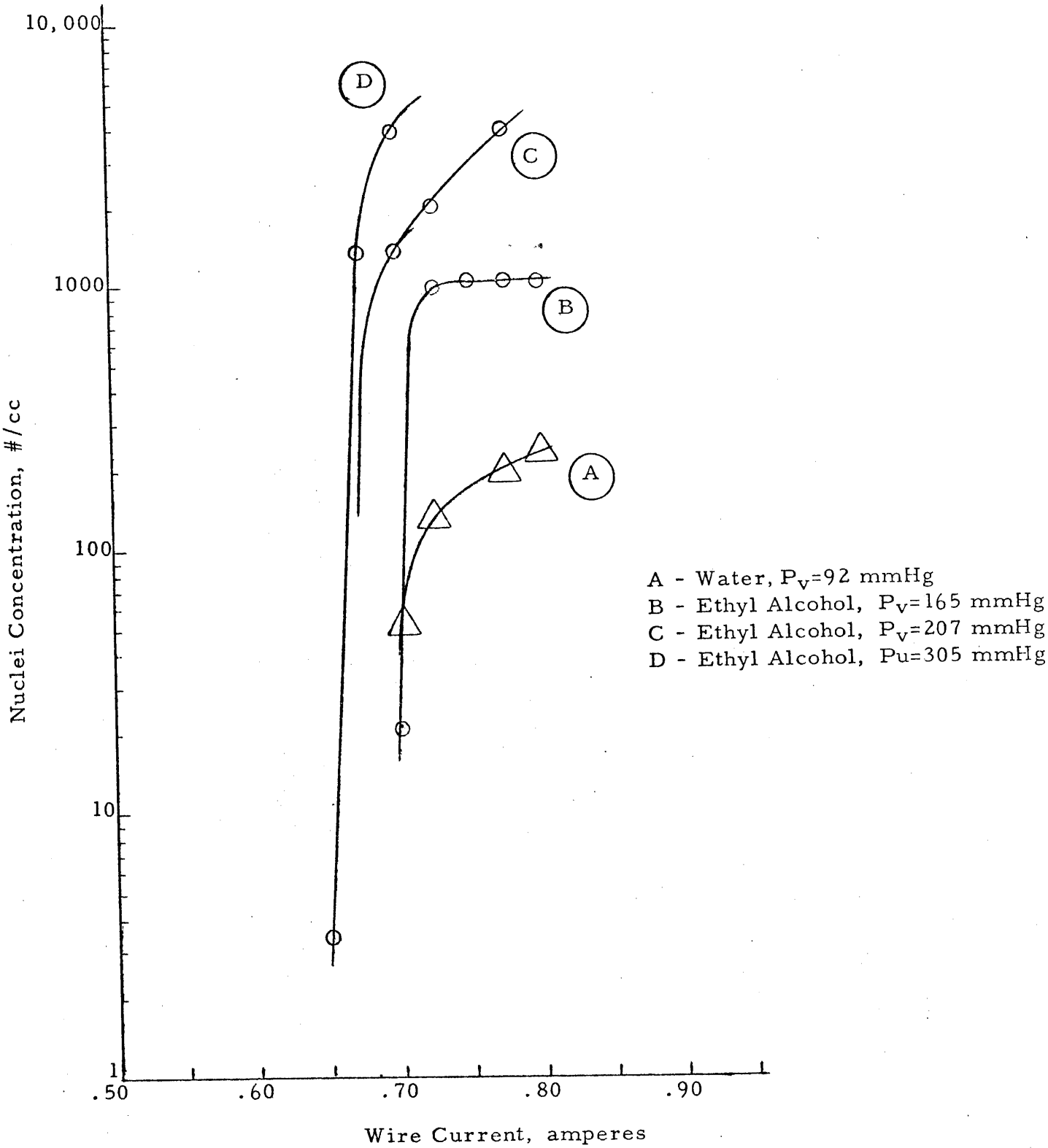

Figure 4. Nuclei Concentration as a function of Wire Current

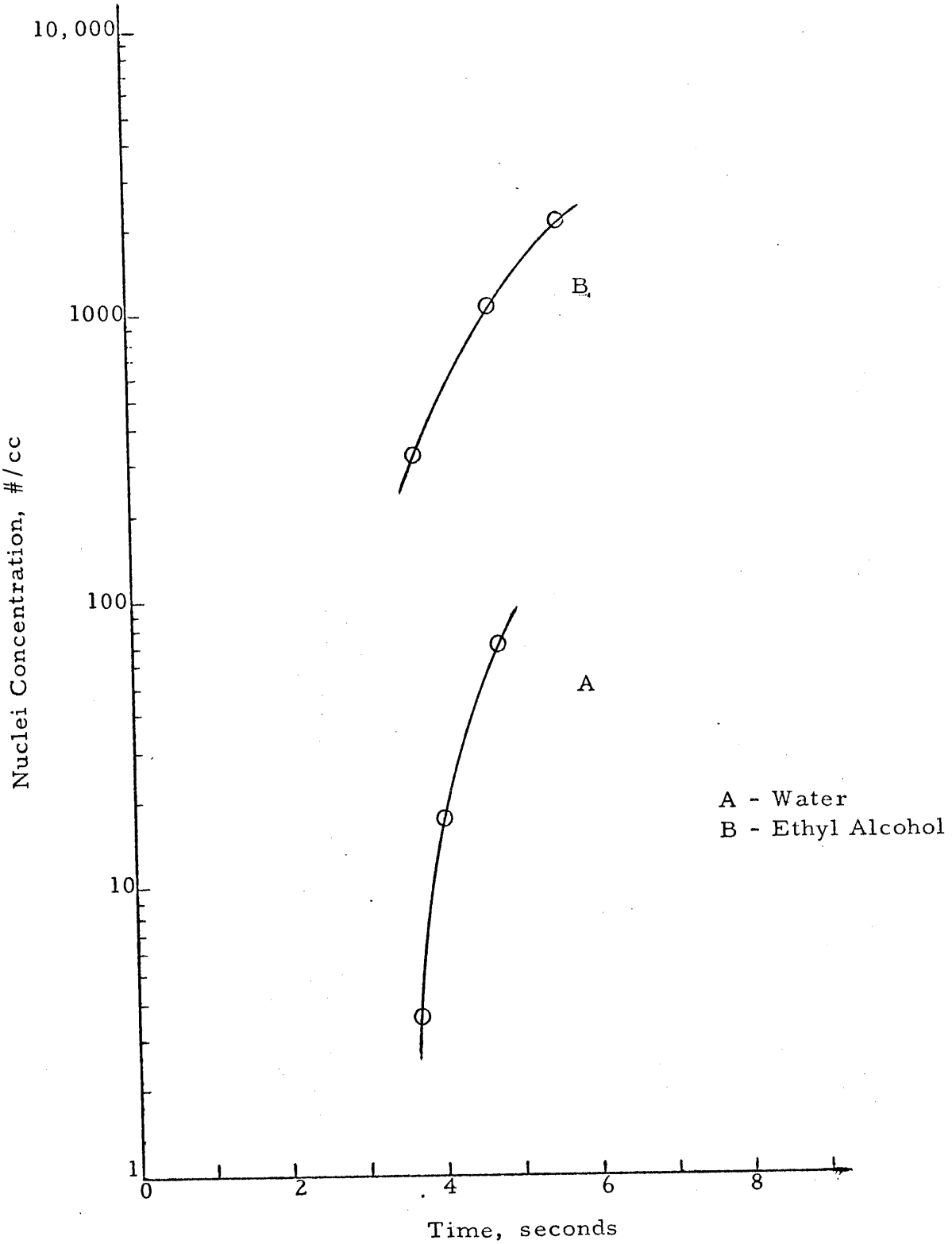

Figure 5. Nuclei Concentration versus Residence Time in Condenser

TABLE 1

Droplet Size Distribution

Droplet Size (microns)	Droplet Concentration (#/cc)
0.5 - 0.7	14
0.7 - 1.4	11
1.4 - 3.0	53
3.0 - 5.0	14
5.0	35

Humidifer Temperature	54.5°C
Condenser Temperature	2.0°C
Wire Current	0.96 amperes

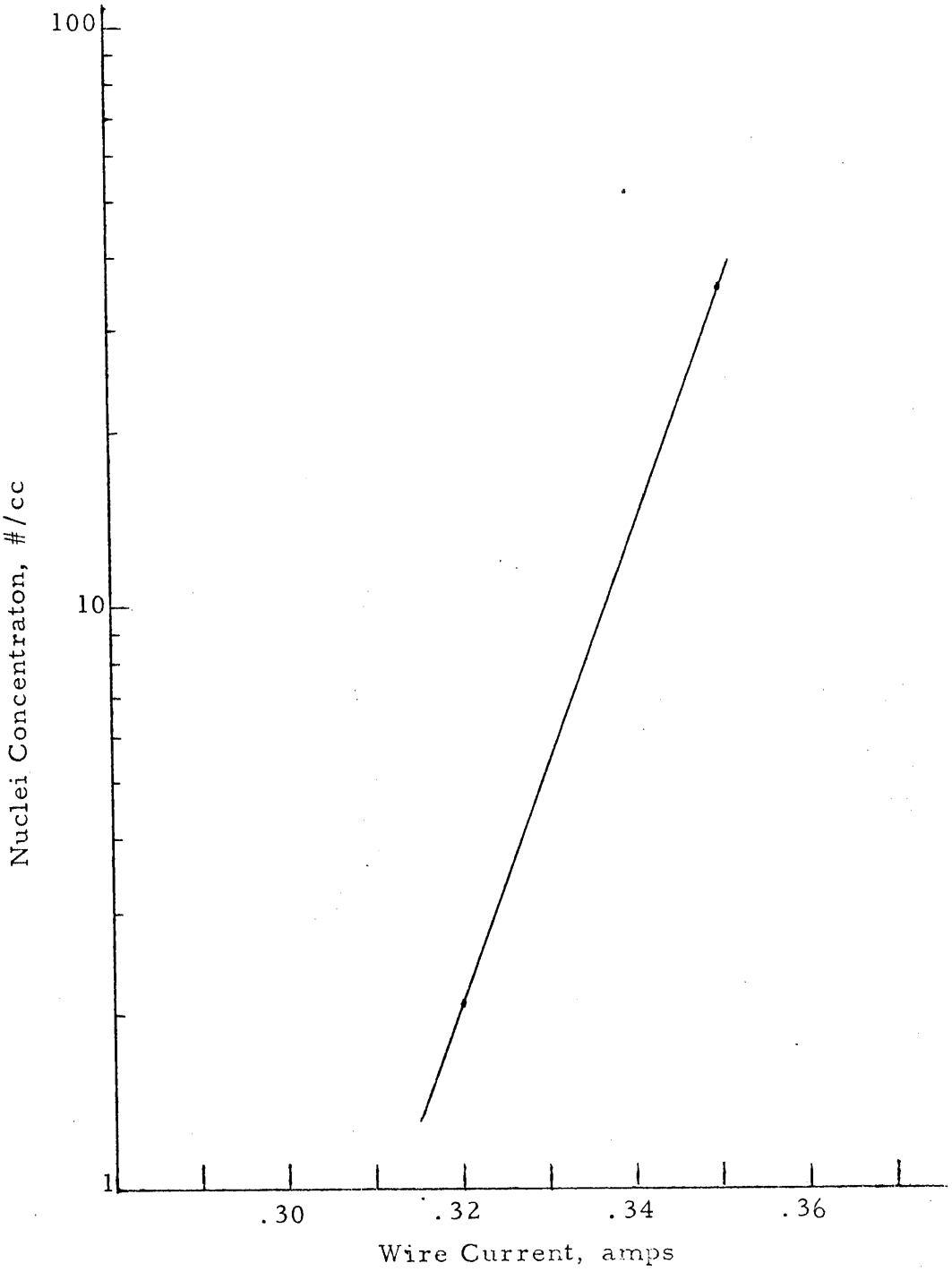

Figure 6. Nuclei Concentration as a Function of Wire Current, NaCl Coated Wire

The salt nuclei were then fed directly to the particle counter to make sure that large NaCl crystals were not being generated. The optical counter did not detect the presence of any particles even at current levels which saturated the condensation nuclei counter; therefore, the nuclei generated were much less than 0.5 micron diameter.

One application for a sub-micron particle counter is monitoring the exhaust of automobiles. The particles of interest are those that are the result of gaseous materials that take part in nuclei and particle producing reactions. For the test, a sampling system, as shown in Figure 7, was connected to the exhaust of a 1972 Ford automobile. The exhaust was cooled, filtered, diluted with clean air and collected in a plastic bag. The nuclei concentration measured at the time of collection was 106/cc. The bag containing the nuclei was placed in the sun for one half hour and the concentration measured again. The concentration measured 2120/cc. The bag was placed in the sun for an additional one half hour and the concentration decreased to 883/cc as shown in Figure 8. The increase in concentration is due to the gaseous reactions occurring in the presence of sunlight producing nuclei. The drop in concentration after one hour is due to agglomeration of particles occurring at a faster rate than production of new particles as the most reactive gases are depleted.

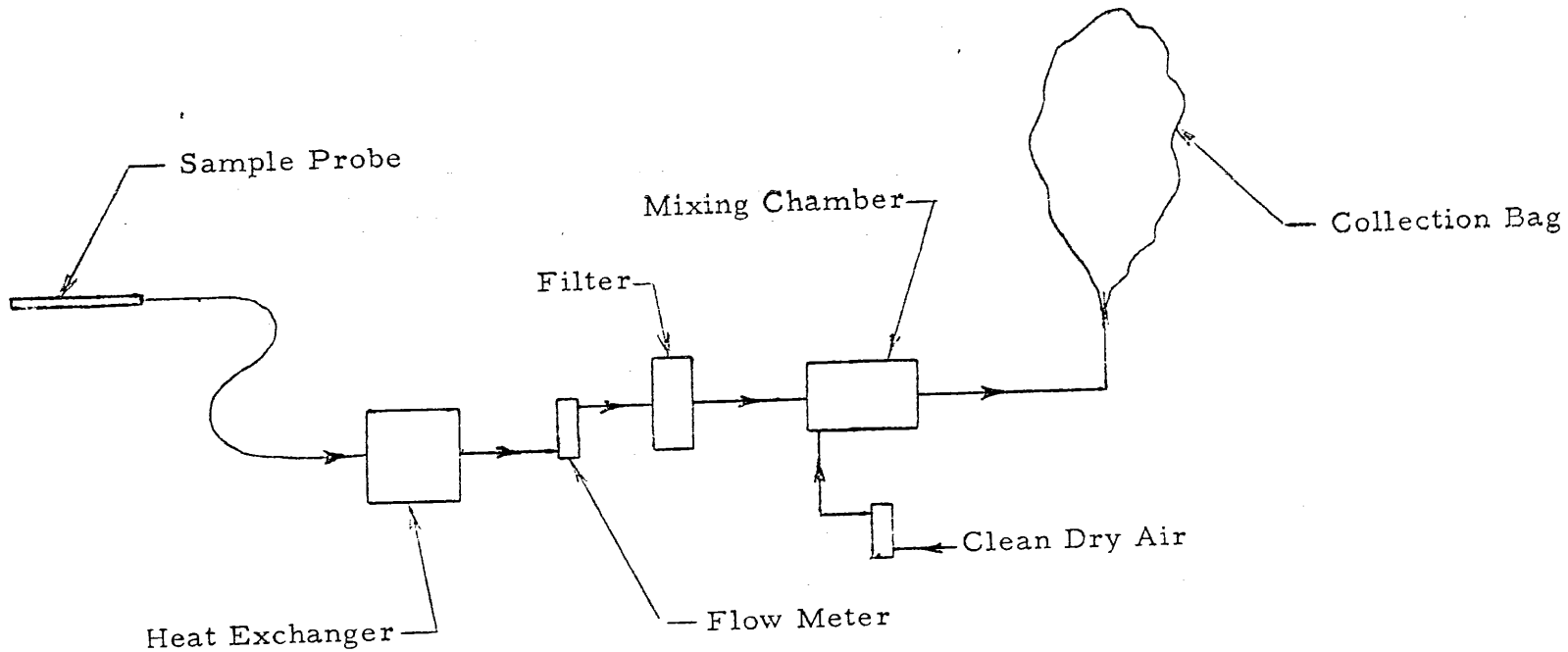

Figure 7. Automobile Exhaust Sample System

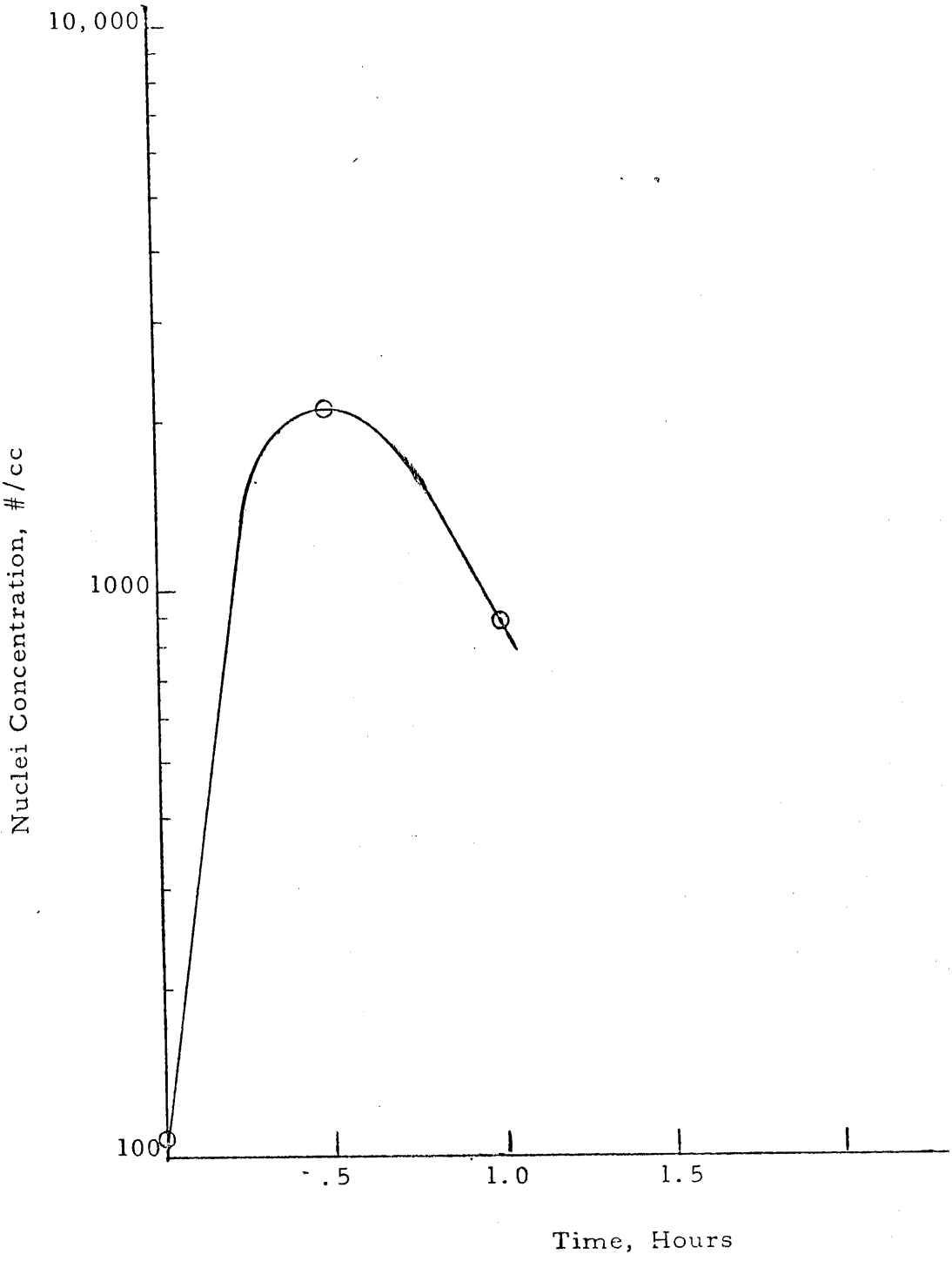

Figure 8. Nuclei Concentration in Filtered Auto Exhaust versus Aging Time

IV - CONCLUSIONS AND RECOMMENDATIONS

It is believed that the primary objectives of this program have been accomplished. We have shown that it is possible to measure the number of particles larger than 0.006μm in diameter in concentrations up to $3x10^3/cm^3$ with no dilution required. Using water vapor as the growth medium, an optimum humidifier vapor pressure for the system geometry is seen to be 125 mmHg; if ethanol is used a vapor pressure of 225 mmHg is suggested. System dimensions were optimized in order to obtain the data reported.

As noted from the data reported, the breadboard hardware does indeed demonstrate feasibility of design. Design validity testing with chromium oxide and with sodium chloride aerosols showed a remarkable difference in performance. Because the fixed humidifier temperature and vapor content is maintained well above the point where any ambient air sample could be found, it is concluded that changes in ambient air temperature and relative humidity do not have any noticeable effect on the operation of the sub-micron particle analyzer.

Some application studies were carried out with automobile exhaust, both before and after irradiation by sunlight. Even though brief, the study indicated the possibility of using the analyzer for study of nuclei-producing reactions, possibly with real time read-out.

Further development can be carried out in either or both of two directions. First, the system that was breadboarded could be developed for delivery to the ARB as a prototype instrument. Second, the breadboard system could be modified further.

The first development would require fabrication of a unified humidifier-condenser-sampler system with automatic temperature control and liquid feed. This sytem would be connected to a standard Royco particle counter, much as the breadboard analyzer was set up. Operation would consist simply of establishing temperatures and sample flow, then determining the nuclei concentration from the particle counter read-out that shows the concentration of droplets grown from the nuclei.

In the second possible development, the condenser section would be modified to include a particle counter optical system. This system would be used to observe the droplets grown from the nuclei before they have reached an equilibrium. The system would require long focal length lenses to avoid condensation on the optical surfaces, along with air sheathing to help keep water from them. A modification such as this could be of value in improving size resolution, since the time for activation after exposure to supersaturation can be associated with nuclei activity.

At your request, we will be happy to give you cost and time allowance for development of the sub-micron particulate analyzer for either development.

References:

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3. Polydorova, M. "Formation and Preparation of Non-Active Condensation Aerosols from Heated Metal Wires" Final Report on Agency Contract R.C. 411 to International Atomic Energy Agency; Institute of Physical Chemistry of the Czechoslovak Academy of Sciences, Prague, Czechoslovakia, August 1970.